INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

XII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLVI. — PYROMETRY: CALIBRATION OF THE LE CHATELIER THERMO-ELECTRIC PYROMETER.

BY SILAS W. HOLMAN.

Presented November 13, 1895.

IN a discussion of thermo-electric interpolation formulæ * the author has shown that the resultant thermal emf. $\Sigma_o^t e$ of a closed metallic circuit of two metals, with one junction at 0° C. and the other at t° C., could be expressed to 0.5 per cent or better above 300° C. by an expression of the form $\Sigma_0^t e = m\, t^n$ or $\log \Sigma_0^t e = n \log t + \log m$, where m and n are constants depending on the metals of the couple. Similar demonstrations show that with the cold junction constantly at 20° C. the emf. may be expressed by $\Sigma_{20}^t e = m\, t^n$ nearly enough. This fact, together with the known fact that the D'Arsonval galvanometer gives readings nearly proportional to the currents, and therefore to Σe on a circuit of constant resistance, led to the thought that the calibration of the Le Chatelier thermo-electric pyrometer might be simplified by the use of a logarithmic instead of a direct plot. A study of a series of six calibrations made at different times by four different sets of observers, with two distinct pyrometers, and in nearly every case with different suspension wires and adjustment, confirmed the deduction and led to the following method. It will be seen that the method requires calibration at only two known temperatures, instead of several, as formerly, — a saving of labor and a gain in accuracy. The method, although suggested by the facts referred to, is not merely a deduction from them. It should rather be regarded as an empirical process based on experiment. It is not rigidly exact, viewed from either a mathematical or experimental standpoint, but is merely an approxi-

* Thermo-electric Interpolation Formulæ, *ante*, p. 193.

mation holding within the limits of variable error of the instrument, and probably well within the limits of uncertainty of the assumed values of the melting points employed in calibration.

For clearness, the usual method of calibration will be first stated, and then the proposed method.

Usual Method.

The cold junction is kept at a temperature usually about that of the room, and measured by a mercurial thermometer. The spot of light is made to read zero with the circuit open. The hot junction is then exposed successively to several known high temperatures, and the scale readings are taken. These temperatures are, ordinarily, the boiling points of naphthalin ($C_{10}H_8$), and of sulphur, the melting points of aluminum, gold, and platinum, — selected as being the most satisfactory in manipulation, and reliable in value. The values assumed for these points differ, following the judgment of the experimenter, Violle's figures 1775° C. for platinum and 1035° or 1045° C. for gold, and Le Chatelier's 625° or 635° for aluminum, being most commonly accepted. From measurements and considerations elsewhere * discussed, the author recommends the following as provisional numbers in preference to the foregoing values.

$C_{10}H_8$	218°.7 + 0.0625 (H–760)	Crafts,† Holman and Gleason.‡
S	444.53 + 0.082 (H–760)	Callendar and Griffiths.§
Al	660.	Holman, Lawrence, and Barr.*
Ag	970.	" " "
Au	1072.	" " "
Cu	1095.	" " "
Pt	1760.	" " "

A plot is then made with deflections (scale readings) as abscissas (horizontal) and temperature differences ($t - c$) between the hot and cold junctions as ordinates (vertical). The points thus obtained lie along a curve which in the upper part approaches somewhat closely to a straight line. But it is nowhere exactly straight, and the error of assuming it so may amount to 10° or 15° or even more. On the other hand the points lie so far apart, if plotted upon a scale com-

* Holman, Lawrence, and Barr, *ante*, p. 219.

† Crafts, Bull. de la Soc. Chim., XXXIX. 196, 277 (1883).

‡ Holman and Gleason, Proc. Amer. Acad., XXI. 237 (1888).

§ Calendar and Griffiths, Phil. Transact., CLXXXII. 119, 157 (1891).

mensurate with the sensitiveness of the instrument, that it is impossible to draw a curve through them which shall be much more reliable in the upper parts (the portion most frequently needed) than the straight line. Although this statement is perhaps counter to others that have been made on the subject, it is the author's opinion, arrived at after prolonged experience with the instrument.

In subsequent temperature measurements this curve is, of course, used for interpolation in the customary manner; that is, any deflection being observed, and at the same time the temperature c' of the cold junction, the plot is entered with this deflection as abscissa, and the corresponding ordinate of the curve is read off. This ordinate will be approximately $(t - c')$ the temperature of the hot minus that of the cold junction. Hence the desired unknown temperature t is obtained approximately by adding c' to this ordinate.

Proposed Method.

Observations. — The scale is adjusted so that the spot reads zero with the circuit open. The cold junction is kept at a temperature about that of the room, and measured by a mercurial thermometer. In careful work this temperature should be kept constant, or nearly so, either at 20°, or, better, at 0° C. The other junction is then exposed successively to two known temperatures, *preferably boiling sulphur and melting copper* (for reasons to be given), or, if temperatures upwards of 1200° C. or 1300° C. are chiefly to be measured, to melting copper and melting platinum. Deflections and temperatures of the cold junction are taken.

Correction for Cold Junction. — If the cold junction is always kept within about one degree of a constant temperature $c°$, e. g. 20° (or 0°), both in calibration and subsequent work, these observed deflections require no correction. If that is not the case, then the deflection should be corrected to obtain what it would have been had this been done. This is readily effected as follows. Let a be the change of deflection per degree at 20° C. This may be found nearly enough by observing once for all the deflection with the cold junction at some observed temperature, anywhere from 10° to 15°, and the hot junction at an observed temperature from 30° to 40°. The deflection divided by the temperature difference will, of course, be a. Then if the observed temperature of the cold junction in a measurement is, e. g., 16° instead of 20°, the correction would be $(20 - 16)\ a = 4\ a$, to be subtracted from the observed deflection, since that was obviously too large. These corrections are small, and can easily be

made mentally, since a is seldom more than one twentieth of a small division of the scale.

Calibration, and Computation of Unknown Temperature. — Let d_s represent the corrected deflection for the sulphur temperature t_s (computed from the reduced barometric pressure H at the time by the foregoing formula) and let d_c be that for the assumed melting temperature t_c of copper or the metal used. Plot two points with log d as abscissa and log t as ordinate respectively. Draw through these two points a straight line. Then within the limits of error of the apparatus, *the ordinate of this line corresponding to any abscissa* log d *will be* log t, *the log of the desired temperature* of the hot junction, d being any observed deflection corrected to 20° or 0° as above. That is, the number corresponding to this logarithm will be t.

By far the most convenient way to effect this plotting and subsequent interpolation, instead of employing logarithm tables and the ordinary co-ordinate or plotting paper ruled with equidistant lines, is to use plotting paper with a logarithmic ruling, that is, with lines spaced at distances progressively diminishing according to the logarithmic law, like the divisions of the ordinary slide rule. By suitably numbering the axes of such a sheet the desired quantities can be plotted directly without the aid of the logarithm tables. Subsequent interpolation then becomes exceedingly easy, since it is merely necessary to enter the plot with the corrected deflection as abscissa, and read off the corresponding ordinate on its numbered axis, this giving directly the unknown temperature t. Unfortunately such paper (which would be useful in many physical and practical problems) is nowhere on sale so far as the author is aware.

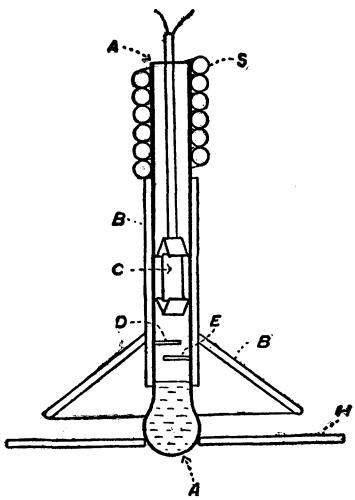
In default of such paper, and instead of using the plot of logarithms for continuous interpolation, a direct reading plot of deflections and temperatures may be made from it once for all. On the logarithmic plot look out the ordinate for every ten (or twenty) divisions of the scale, i. e. corresponding to log 10, log 20, log 30, etc. (smallest divisions). Look out in the log tables the numbers corresponding to these ordinates, thus obtaining t_{10}, t_{20}, etc. Make a new plot, with 10, 20, 30, etc. as abscissas, and t_{10}, t_{20}, t_{30}, etc. as just found, as ordinates. These points can be taken at such short intervals that a reliable smooth curve may easily be drawn through them, and this is then available for subsequent direct interpolations.

In the absence of logarithmic plotting paper, log plots may very conveniently be made by a straight edge, graduated with a logarithmic scale. Four of such rulers (two of single and two of double scale)

may be cut from an ordinary boxwood slide-rule by a skilful carpenter. They are very useful in a variety of physical work, but less so than the ruled paper.

Proof of the Method. — The method rests for demonstration on the fact that logarithmic plots thus made for the six calibrations above cited, each containing observations on naphthalin, sulphur, aluminum, gold, and platinum, and using the above temperatures, were straight lines well within the limits of variable error of the observations with but one exception, when the platinum point showed a wide divergence, presumably due to mistake, or possibly to faulty setting up of the instrument.

Apparatus and Procedure in Calibrating: Sulphur. — For this boiling point, in order to obtain as good results as the instrument is capable of, the boiling point tube shown in the sketch is satisfactory, and a duplicate serves well for naphthalin. The glass tube is about an inch in diameter, and twelve inches long, terminating below preferably in a bulb about two inches in diameter. The tube, to within two inches of the top, is wrapped with asbestos cloth of a thickness of at least a quarter of an inch, to prevent radiation and superheating. An asbestos cover closes the top. The clear part of the tube serves as a condenser, which may be made more efficient by a spiral coil of wire, *S*. It is easy to regulate the rate of boiling so that the visible line of condensation in the tube is nearly steady in position. The bulb rests on a diaphragm of asbestos board, having an opening about half an inch smaller in diameter than the bulb. The whole apparatus is supported in a clamp stand. The flame plays upon the bulb where it is exposed by the hole, but the diaphragm (six or eight inches in diameter) prevents the hot gases from passing up around the tube, which would cause superheating. Two overlapping diaphragms, *D* and *E*, about an inch above the sulphur and half an inch apart, prevent spattering and radiation from the liquid to the thermal junction. The wires of the couple extend downward through the cover to a



point an inch or less above the diaphragm. The sulphur should extend from the bulb to a point half an inch or more into the tube. It will usually be found necessary to pour out the liquid sulphur at the close of a calibration to avoid breaking the tube at the next heating. If there is trouble from breaking of the tube during boiling (none with good glass) a wire copper gauze wrapped about the bulb will be found a preventive. The boiling should be maintained for a few minutes after the sulphur vapor has risen above the top of the asbestos to insure uniformity of temperature. It is advantageous to put the wires through a small hood, or umbrella of asbestos at a point about an inch above the junction, so shaped as to shed the drip of cooler liquid sulphur which will run down the wires. A special form of this hood is shown at *C* in the figure. Both this and the diaphragms in the tube are, however, unnecessary in ordinary work.

For comparatively rough work it is sufficient to boil some sulphur in an ordinary or small test tube (about one fourth full) and hold the junction at the surface of the boiling liquid, taking pains not to have it touch the tube, and also not to overheat the tube. This is the customary procedure, but is not quite worthy of the instrument.

The barometer and its temperature should be observed at the time and place of making the calibration, although the errors from omission of this are negligible in rough work.

Copper. — The high grades of commercial copper are good enough* for this use; such, for example, as are used in the best rolled sheet copper and wire. This, of course, is easily obtainable and inexpensive, and may probably be relied upon as having a melting point not much, if any, over 1° C. below that of pure copper. Electrolytic copper of a much higher grade of purity is preferable, and is not now rare or expensive.

A fire clay crucible,† $1\frac{1}{4}$ to $1\frac{1}{2}$ inches deep, and about 1 inch in diameter, is held in place inside a small furnace by pieces of fire-clay, as shown on page 240. A double-walled furnace of the design and proportions shown ‡ (the figure is half size) is most satisfactory. It is about $4\frac{1}{2}$ inches outside diameter, and $3\frac{1}{2}$ inches high. The crucible contains upwards of fifty grams of copper. Above this, within

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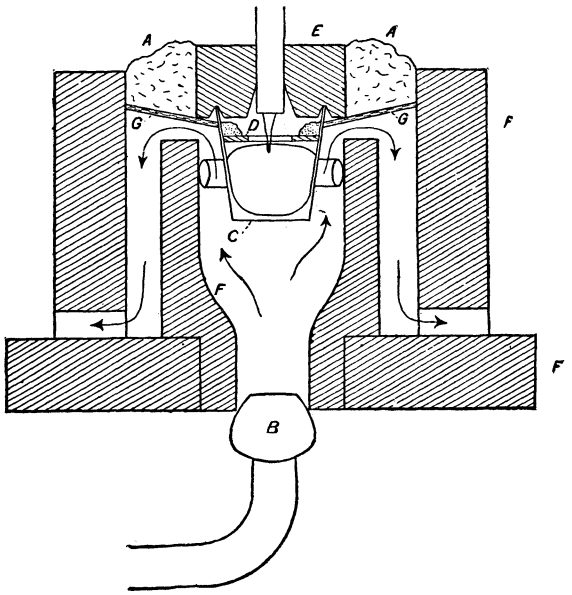
* See results by H., L., and B.

† Buffalo Dental Co., Buffalo, N. Y.

‡ Wiesnegg, also Carpentier, both of Paris, supply such a furnace; or one may readily be made by any manufacturers of fire-clay apparatus. The Fletcher furnaces may also be used but are not so convenient for the purpose because the products of combustion escape at the top.

the crucible, is a diaphragm, *D*, made from a plate of battery carbon. It has a central perforation large enough to permit the passage of the clay tube carrying the thermo-couple. Upon this diaphragm is placed powdered charcoal. A block, *E*, of battery carbon is turned to fit the rim of the crucible somewhat closely to serve as a cover. *G* is a diaphragm of asbestos board which deflects the gases, and upon this at *A* is placed fibrous asbestos to reduce the heat conductivity. The cover belonging to the furnace is not used. Simpler details might serve sufficiently well, but they must effect the same result,



namely, to produce by slow combustion an atmosphere of carbon dioxide in the crucible to retard the oxidation of the copper. As above arranged, the powdered charcoal does this, and the carbon plates do not burn.

The thermo-couple projects as shown into the metal, being of course thrust in during the first melting. It is obviously indifferent whether the wires are joined or not. The end of the wires will require clipping subsequently, to remove the short section injured by action of the copper. The uniformity of the wire, however, renders this a source of no sensible error.

The apparatus being arranged as shown, and the copper liquefied

(it should not be unduly superheated), the blast is slightly reduced so that the crucible may cool slowly, and the pyrometer is read continuously. When the solidifying point is reached, the reading will become constant for some minutes (dependent on the rate of cooling) and will then begin to descend. This "steady point" occurs, of course, during the absorption of the latent heat, and is the desired reading corresponding to the solidifying point. The blast is then increased, and the corresponding constant reading in the ascending temperatures gives the melting point. This should, with copper, be sensibly coincident with the solidifying point, and will be found so unless complications are introduced, through too rapid heating or cooling, or through the formation of slag upon the top of the copper. It is well to withdraw the junction, clean it if necessary, and take check readings.

The advantages of copper over gold, as demonstrated elsewhere,* are that it is more easily and cheaply obtainable in a state of purity insuring a reliable melting point, and that, by using a large mass, an unmistakable steady reading of considerable duration can be obtained. The latter consideration is of special weight where the galvanometer is exposed to jarring, or the observer is not experienced. The operation is no more laborious, and, except possibly for a skilled observer, is less time-consuming, and more satisfactory than the customary method with gold.

In Le Chatelier's original method of employing gold (or other metals) this same furnace was used, but with its cover on. The crucible, without a cover, was filled with magnesia or lime, and the thermal wires, passing through a perforation in the furnace cover, terminated with their junction in the centre of the crucible, surrounded by the magnesia. Before its insertion the junction was carefully wrapped with a small piece of wire or foil of gold, or of any metal under test. This being arranged, the blast was controlled to raise the temperature at a slow and steady rate. The spot of light on the pyrometer scale was then watched closely. It would be seen to advance steadily until a certain point was reached, then to stop abruptly for a moment, then to start upward again almost with a bound and go on rising. This temporary stopping was due to the time required for the absorption of the latent heat of fusion. A similar stopping point may then be generally observed on allowing the furnace to cool slowly. These two points, the "melting and freezing points," should

* See former reference to H., L., and B.

in general agree. With too rapid rates of heating or cooling, they are likely to show an erroneous disagreement. Under favorable conditions, namely, with the galvanometer in a place free from jarring, and with a steady air-blast of quite sufficient capacity, this method yields perfectly good results, although the inexperienced observer will generally miss the reading on the first one or two trials. But in most places, notably in connection with industrial plants, it is not infrequently difficult or impossible to secure the necessary steadiness of support or of blast. Failing these, the stopping point sought is very likely to be so masked by irregularities in the motion of the spot as to introduce much uncertainty into readings, if not entirely to prevent satisfactory calibration by this method.

Another way is to have the two thermal wires held together at the ends merely by the wrapping of gold, etc., and under slight tension, so that as soon as the metal melts the wires will draw apart and open the circuit. The spot will then reach a highest point corresponding to the melting point, and then suddenly drop to zero. In practice this method, although convenient in some cases, has been found not to yield satisfactory results on the whole.

With some metals, particularly those melting below gold, the author has found the following arrangement to work well, being more rapid and under better control. A small crucible of fire-clay, $1\frac{1}{2}$ or 2 inches long, and $\frac{1}{4}$ to $\frac{3}{8}$ inch inside diameter, with straight sides and a flat bottom, is employed.* Into this is inserted the clay tube carrying the wires, a packing of asbestos being used around it, if it does not pretty well fit the crucible. The junction remains free about half an inch from the bottom and not touching the sides. The crucible is then gradually heated in the flame of the blast lamp, and the stopping point observed as before.

Platinum. — For this we depend on the direct fusion of the platinum wire of the couple just at the junction.† A convenient way is to fuse the ends together, then to bend the wires so that the two lie closely side by side, and are nearly straight, but not touching. Then lay the end on a smooth surface of quicklime. A small flame from the oxyhydrogen blowpipe is then directed upon the junction. The globule at the end will fuse, and may gradually work up along the

* Made to order by Hall and Sons, Tonawonda St., Buffalo, N. Y.

† It may be of interest to others, as it was to the writer, to learn that the firm of Heraeus of Hannover, Germany, which has made platinum of exceptional purity for the Reichsanstalt, has an agency in New York, Charles Englehard, 41 Cortland St., N. Y.

wires. By watching the surface appearance of the globule closely, it is easily possible to control the position and effect of the flame so as to maintain the mass just on the point of fusion and get a fairly constant reading. Heavily clouded dark glasses *must* be used in watching the platinum. Neglect of this involves risk of serious permanent injury to the sight, and, if persisted in, of even greater danger.

Modifications of the Le Chatelier Thermo-electric Pyrometer. — By an experience extending over four years in the use of this instrument in its original form, and after tests and study of many other forms of pyrometer, the writer is convinced both that the thermo-electric method is by far the most promising one as the basis for industrial pyrometer, as well as for much measurement in scientific research, and that the Le Chatelier form of the instrument is the most generally satisfactory one now obtainable on the market. Yet for general industrial services the Le Chatelier instrument falls short of the requirements in two ways. First, it is not sufficiently simple of manipulation in the setting up, and in the calibration, to be put into the hands of any but a fairly well trained observer. A trained chemist of works, an educated superintendent, or any man of such caliber may be expected to take the instrument as sent by the makers, mount it, and operate it successfully ; and under such observers it is doing important service in many places. The mere reading can be done by any foreman after a few words of explanation. Secondly, the conditions of support requisite for the galvanometer, although often obtainable, are by no means commonly to be found in those portions of industrial works where it would be otherwise advantageous to locate the instrument. These facts are restricting the introduction of an instrument otherwise excellent in its performance and marking a distinct onward step in the art of practical pyrometry.

The urgent need of a still more universally practicable pyrometer cannot be too strongly nor too often emphasized. In a large number of industrial processes of great magnitude the employment of a reliable pyrometer would certainly result in a notable advance in quality of product, in prevention of waste, in improvement or perfection of the process itself, and in the discovery of new methods and new products. If a galvanometer as reliable, as simple, and as portable as the Weston magnetic voltmeter could be directly connected to a rhodo-platinum thermal couple, there would result, as I have for some years urged, an almost ideal pyrometer for technical work. Thus far, unfortunately, the Weston instruments do not yield in this combination sufficient sensitiveness to admit of their being put forward as meeting

any but very special needs. Nevertheless, at least one such combination is said to have been successfully used for a certain purpose. The writer has made repeated efforts to obtain a suitable instrument from the Weston Company, and from some others, without success.

Rogers Laboratory of Physics,
Massachusetts Institute of Technology,
Boston, September, 1895.

NOTE.

A portable form of D'Arsonval galvanometer, combined with a rhodo-platinum thermo-couple and graduated in degrees up to 1500° C., is now announced by Keiser and Schmidt of Berlin.* Its graduation is based upon the investigations of Holborn and Wien at the Reichsanstalt.

The author desires, also, to call attention to the convenience of maintaining a constant calibration curve for the Le Chatelier pyrometer by the insertion of an adjustable resistance in the circuit. By this means the unavoidable slight changes of resistance of the circuit, of sensitiveness of the galvanometer, and even of electro-motive force of the couple, can be readily offset. The procedure would, of course, be to adjust the resistance until the sulphur or the copper reading was the same as in the original calibration. S. W. H.

* Zeitschrift für Instrumentenkunde, XV. 285 (August, 1895).